



REC'D 15 AUG 2003

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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 9 July 2002 with an application for Letters Patent number 520070 made by Canterprise Limited.

I further certify that pursuant to a claim under Section 24(1) of the Patents Act 1953, a direction was given that the application proceed in the name of SYFT Technologies Limited.

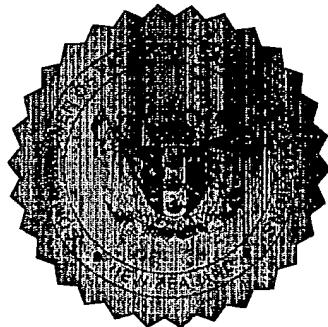
Dated 23 July 2003.

PRIORITY DOCUMENT

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A handwritten signature in black ink that reads "Neville Harris".

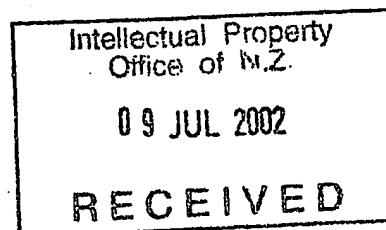
Neville Harris
Commissioner of Patents



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SUBSTITUTION OF APPLICANT
UNDER SECTION 24

10



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20 Patents Form No. 4

Patents Act 1953

PROVISIONAL SPECIFICATION

IMPROVED METHOD OF ANALYSIS

25 We, Canterbury Enterprise Limited, a New Zealand company of University of Canterbury, Private
Bag 4800, Christchurch, New Zealand, do hereby declare this invention to be
described in the following statement:

Title: Improved Method of Analysis

TECHNICAL FIELD

5 The present invention relates to a method for detecting any of a number of substances present in gases or gas mixtures containing alkanes, ethene or ethyne, using chemical ionization mass spectrometry.

10 The invention is especially useful for detecting leaks of gas from gas lines or gas containers:- producers of gas often add substances containing sulphur or other odiferous material to gas to aid the detection of leaks, and it is very useful to be able to detect small leaks, i.e. very small quantities of the sulphur-containing or other added material. For this, it is necessary to have a detection method which reacts with the sulphur-containing or other added material but does not react with the bulk gas or with the major constituents of air.

15 However, it will be appreciated that the invention is not restricted to this particular use, but is useful also in a variety of other applications.

BACKGROUND ART

20 Chemical ionization mass spectrometry has been used for analyte identification since the development of mass spectrometry [Munson, M.S.B.; Field, F.H. *J. Amer. Chem. Soc.*, 88, 2621 – 2630, (1966); Munson, M.S.B.; Field, F.H. *J. Amer. Chem. Soc.*, 88, 4337 – 4345, (1966); Munson, M.S.B.; Field, F.H. *J. Amer. Chem. Soc.*, 89, 1047-1052, (1967)]. In recent years instruments utilizing chemical ionization sources have been marketed for analysis of gas mixtures [Linforth, R.; Preece, S. Technical Note 236, Micromass Ltd, (1998); Adechy, M.; Shiess, V.; Squibb, A. *Peak*, 1, 2-4, (2000)]. The combination of a chemical ionization source with flow tube reactor techniques allows both identification and quantification of trace species without internal calibration.

25 Two closely related systems have been developed using this combination of techniques; *proton transfer mass spectrometry* [Lindinger, W.; Hansel, A.; Jordan, A. *Int. J. Mass Spectrom. Ion Proc.*, 173, 191-241, (1998)] and *selected ion flow tube mass spectrometry* [Spanel, P.; Smith, D. *Med. Biol. Eng. Comput.*, 34, 409-419, (1996)].

30 35 The selection of the chemical ionizing agent or precursor ion is critical to the

application of the technique. The precursor ion must be reactive with the analyte molecule(s) but unreactive with the bulk gas within which the analyte is present as a trace component. In most applications to date the bulk gas is ambient air or exhaled breath and the analyte species are various Volatile Organic Compounds (VOCs).

5 Precursor ions which have been in common use include NO^+ , O_2^+ , NH_4^+ and OH^- . A further important criterion for selection of a chemical ionization precursor is the facility with which it can be generated in large amounts using typical instrumentation such as an electron impact or microwave discharge source.

10 It is known from previous experimental work (Freitas, M. A., O'Hair, R. A. J. Int. J. Mass Spectrom. Ion Proc. 1998, 175, 102-122) that the methoxymethyl cation is not reactive with alkanes, but will react with molecules containing heteroatoms. However, the use of $\text{CH}_3\text{OCH}_2^+$ as a chemical ionization reagent for quantification and identification of analytes has not been tried previously.

15

DISCLOSURE OF INVENTION

The present invention provides a method of detecting and quantifying trace levels of molecules containing one or more of a range of reactive species, in gases or gas mixtures consisting of alkanes, ethene, or ethyne, said method including using an 20 alkoxyalkyl cation as the chemical ionisation precursor in a mass spectrometer.

Preferably, said method further includes reacting the sample gas to be analysed with the alkoxyalkyl cation in a flow tube, in a stream of helium.

25

The range of reactive species includes molecules that contain sulphur, nitrogen, oxygen, phosphorus or silicon heteroatoms.

30

To date, the experimental work has been carried out using the methoxymethyl cation, but it is believed that other alkoxyalkyl cations could be used instead.

BRIEF DESCRIPTION OF DRAWINGS

35 By way of example only, a preferred embodiment of the present invention is described in detail with reference to the accompanying flow chart.

BEST MODE FOR CARRYING OUT THE INVENTION.

Referring to the flow chart, in step 1, a supply of methoxymethyl cations is produced.

5 This may be done by any of a number of known methods:- for example, using the helium flowing afterglow method in which a stream of helium gas is passed in a pyrex or quartz tube through a microwave discharge and a small amount of dimethoxymethane is added to the gas stream emerging from the tube. Methoxymethyl cations are produced by a reaction between the helium metastable species and the dimethoxymethane.

10 Another process which may be used to produce the methoxymethyl cations is electron impact using an incandescent rhenium filament within a vacuum chamber filled with a low pressure dimethoxymethane.

15 In step 2, the methoxymethyl cations are mass selected, using a mass spectrometer.

In step 3, the methoxymethyl cations are introduced into the inlet of a flow tube in a carrier flow of helium, at ambient temperature and at a pressure of about 0.5 Torr.

20 As the mixture of helium and methoxymethyl cations flow along the flow tube, the sample gas to be analysed is introduced into the flow tube via a capillary inlet (step 4).

25 In step 5, the methoxymethyl cations react with the gas sample, which is primarily one or more alkane gases, but which also contains traces of molecules containing heteroatoms, (e.g. sulphur, nitrogen). This type of gas sample is typical of the type of sample from a leaking gas pipe.

30 The methoxymethyl $[\text{CH}_3\text{OCH}_2^+]$ ion is unreactive with alkanes, ethene and ethyne, i.e. the hydrocarbons that are present as bulk constituents of natural gas and other hydrocarbon fuel mixtures viz methane, CH_4 ; ethane, C_2H_6 ; propane, C_3H_8 ; butane, C_4H_{10} ; ethylene, C_2H_4 and acetylene, C_2H_2 . The $\text{CH}_3\text{OCH}_2^+$ ion is, however, reactive with many sulfur-containing and nitrogen-containing species, including methanethiol, CH_3SH ; ethanethiol, $\text{C}_2\text{H}_5\text{SH}$; dimethylsulfide, $(\text{CH}_3)_2\text{S}$ and diethylsulfide, $(\text{C}_2\text{H}_5)_2\text{S}$.

The reactivity of $\text{CH}_3\text{OCH}_2^+$ with selected neutral species in a pressure of 0.5 Torr of helium at room temperature is shown in Table 1.

Table 1. Reactivity of $\text{CH}_3\text{OCH}_2^+$ with selected neutrals.

Neutral	Products	Branching Ratio	Reaction Rate ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)
O_2	No reaction		<0.0005
N_2	No reaction		<0.0005
H_2O	No reaction		<0.0005
CO	No reaction		<0.0005
CO_2	No reaction		<0.0005
Ar	No reaction		<0.0005
CH_4	No reaction		<0.0005
C_2H_6	No reaction		<0.0005
C_3H_8	No reaction		<0.0005
C_4H_{10}	No reaction		<0.0005
C_2H_2	No reaction		<0.0005
C_2H_4	No reaction		<0.0005
CH_3SH	$\text{CH}_3\text{OCH}_2\text{CH}_3\text{SH}^+$ $\text{CH}_3\text{SHCH}^+ + \text{CH}_3\text{OH}$	(0.95) (0.05)	0.31
$\text{C}_2\text{H}_5\text{SH}$	$\text{CH}_3\text{OCH}_2\text{C}_2\text{H}_5\text{SH}$ $\text{C}_2\text{H}_5\text{SHCH}^+ + \text{CH}_3\text{OH}$	(0.15) (0.85)	0.90
$(\text{CH}_3)_2\text{S}$	$\text{CH}_3\text{OCH}_2(\text{CH}_3)_2\text{S}^+$ $(\text{CH}_3)_2\text{SCH}_3^+ + \text{HCHO}$	(0.95) (0.05)	1.4
$(\text{C}_2\text{H}_5)_2\text{S}$	$\text{CH}_3\text{OCH}_2(\text{C}_2\text{H}_5)_2\text{S}^+$	(1.0)	1.9

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The reacted gas sample produced in step 5 is then analysed in known manner in a mass spectrometer (step 6). Since the methoxymethyl cations react only with the molecules containing the heteroatoms, analysis of the mass spectrometry results can be used to calculate the concentration of the trace species containing heteroatoms present in the alkane gases.

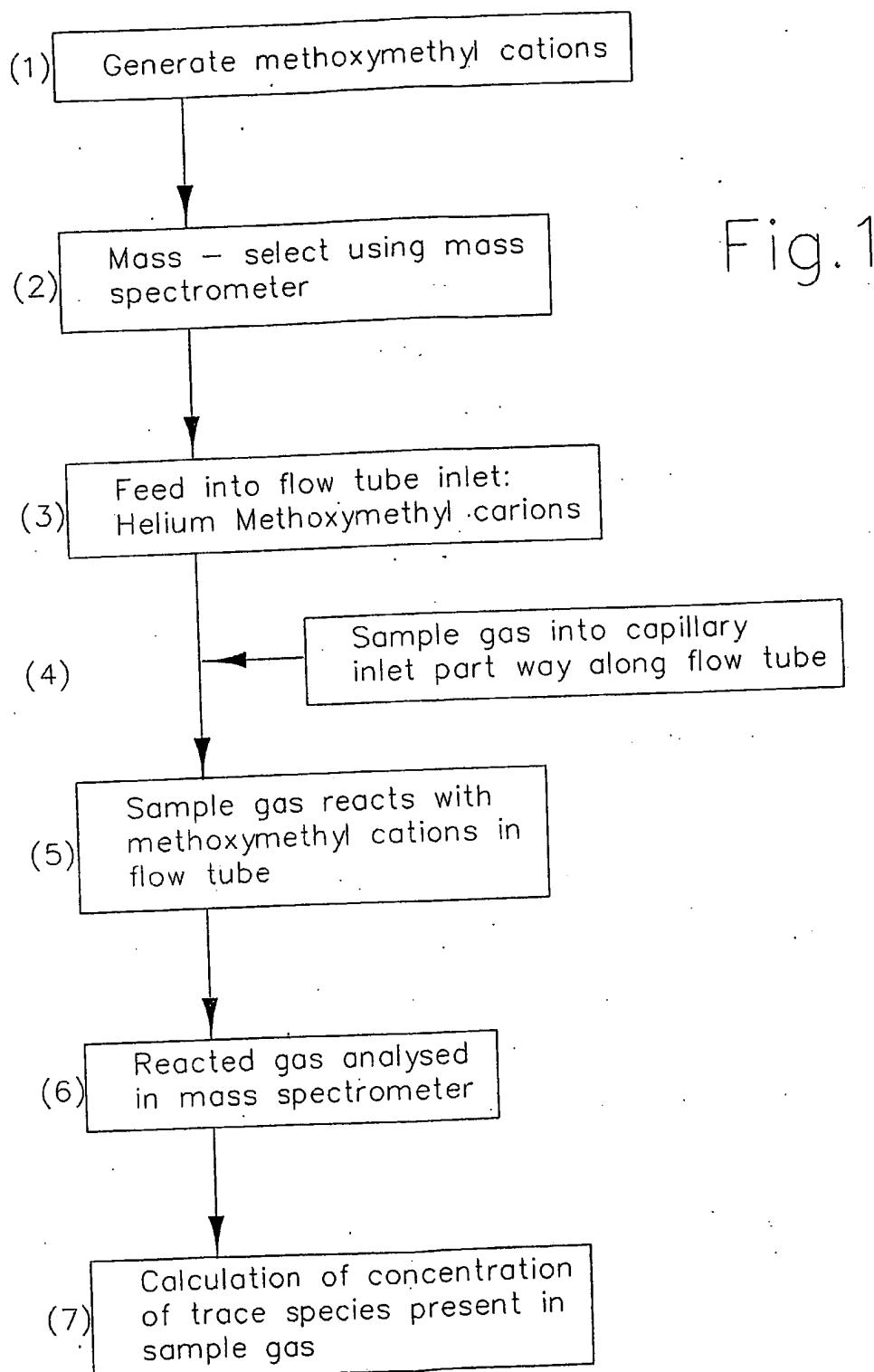


Fig.1